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SYNTHESIS OF SILANE AND SILICON IN A NON-EQUILIBRIUM PLASMA JET

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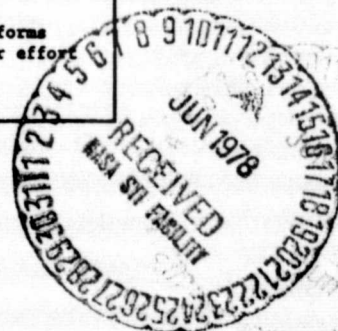
FIFTH QUARTERLY REPORT

H.F. CALCOTE AND W. FELDER

DECEMBER 1977

This work was performed for the Jet Propulsion Laboratory, California
Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy
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AeroChem Research Laboratories, Inc.
Princeton, New Jersey

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AeroChem **Research Laboratories, Inc.**
Princeton, New Jersey

FOREWORD AND ACKNOWLEDGMENTS

This is the fifth quarterly progress report on a program which started 20 July 1976; it covers the period 21 June 1977 to 31 October 1977.

During this report period the following people made significant contributions to the program: R.L. Revolinski, R.H. Mullen, R.D. Thorpe, and H.N. Volltrauer.

ABSTRACT

The objective of this program is to determine the feasibility of using a non-equilibrium hydrogen plasma jet as a chemical synthesis tool in helping to meet the objectives of the JPL Low-Cost Silicon Solar Array Project. Reactions of hydrogen atoms (produced by a glow discharge and expanded through a nozzle) with chlorosilanes are being studied.

During this period, our previous results were evaluated and four possible processes identified for further study: (1) production of polycrystalline silicon photovoltaic surfaces, (2) production of SiHCl_3 from SiCl_4 , (3) production of SiH_4 from SiHCl_3 , and (4) purification of SiCl_4 by metal impurity nucleation. Estimates, based on homogeneous and wall recombination rates, indicate that the hydrogen atom concentration far downstream of the nozzle at the liquid nitrogen traps is less than 20% of its original value. This could account for the low yields, about 10% of SiCl_4 converted to SiHCl_3 collected in the traps, but does not explain the failure to observe reactions of SiCl_4 in the gas phase. In situ mass spectrometric measurements using SiHCl_3 indicated about 30% SiHCl_3 consumption; SiH_4 was qualitatively identified as a gas-phase product. Previous difficulties with the mass spectrometer have been corrected and these questions can now be addressed more accurately.

The most striking result was the recognition that the strongly adhering silicon films, amorphous or polycrystalline, produced in our studies could be the basis for preparing a photovoltaic surface directly; this process has potential advantages over other vapor deposition processes. Strongly adhering films of amorphous and polycrystalline silicon have been laid down on Pyrex and Vycor using SiCl_4 or SiHCl_3 as reactant; SiH_4 produced a loose powder. These films are stable up to temperatures of 1200 K (on Vycor) except for cracking, and upon heating undergo a change to a more metallic appearance, presumably associated with a change from amorphous to polycrystalline silicon. These observations must be substantiated by more sophisticated analysis. To date, with no attempts at optimization, the maximum conversion efficiencies (mol % reagent to product silicon) observed for film formation are: SiHCl_3 17%, SiCl_4 (technical) 8%, SiCl_4 (semiconductor) 3%, and SiH_4 (powdery film) 7%. Film thicknesses up to 20 μm have been prepared. Heavy films crack and peel.

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I. INTRODUCTION

The objective of this program is to determine the feasibility of using a non-equilibrium hydrogen plasma jet as a chemical synthesis tool for meeting the objectives of the JPL Low-Cost Silicon Solar Array Project. The rationale behind the approach being pursued was outlined in the first quarterly report.¹ Small concentrations of H atoms, about 3% in H₂, at a high flux are produced at an energy utilization efficiency of about 30% in a glow discharge.² Expansion through a nozzle produces an H/H₂ jet which is reacted with a chlorosilane (SiCl₄ or SiHCl₃) to produce a lower silane or silicon. SiH₄ might also be used as a reactant to produce silicon.

During the reporting period the results previously reported¹⁻⁴ have been evaluated to determine four potential processes which should be given further consideration. One of the original objectives, producing SiH₄ from SiCl₄ does not appear feasible; reaction rates in the gas phase appear to be slow for SiCl₄--the main reactions occurring on surfaces. More recent experiments, however, (see Section II.C) indicate that SiH₄ may be produced in the gas phase for SiHCl₃. Theoretical estimates have been made of the rate of H-atom decay through the apparatus; it may be necessary in the future to confirm these results should we attempt to obtain rate constants from our observations. Problems associated with the mass spectrometer have been resolved. The major effort during this period was directed to studies of the solid films deposited on the reactor walls. Several series of experiments were made in which the variation in the nature of the film with experimental conditions was observed. Experiments included heating the films to as high as 1200 K in an inert gas atmosphere. Some limited conclusions can be drawn from such studies, though only a few simple analytical techniques were used, principally visual examination using a metallurgical microscope. The film studies suggest the possibility of a new vapor deposition process for preparing silicon photovoltaic cells.

II. TECHNICAL DISCUSSION

A. POTENTIAL PROCESSES

Since the objective of this program is to determine the feasibility of using a non-equilibrium hydrogen atom plasma jet in the production of silanes or solar grade silicon, it was desirable at this point to examine which plasma jet processes appear most favorable in the light of the work to date. The original effort was directed toward converting SiCl_4 to SiH_4 or a lower chlorosilane. To date SiH_4 has been produced in only very small concentrations, $\approx 2\%$ of reactant SiCl_4 ,² and then apparently mainly on the surface of liquid nitrogen traps. This process does not look attractive.

The following possible processes, however, merit further exploration:

1. Production of polycrystalline silicon from the reaction of SiCl_4 , SiHCl_3 , or SiH_4 with the H/H_2 jet. In the present experiments some solid deposits have been analyzed as silicon and photomicrographs of these solids have been interpreted as evidence for the presence of polycrystalline silicon or under special experimental conditions, polymer or amorphous silicon.³ In work during this reporting period reasonable yields of silicon have been obtained, but the conditions determining the nature of the deposit have not been completely defined. Since the films often adhere very strongly to the Pyrex or Vycor substrates, the possibility exists of using the technique for preparing the photovoltaic surface directly. Such a simple process could offer several advantages over chemical vapor deposition (CVD) of polycrystalline silicon as it is often carried out.⁵ The substrate temperature in the present studies has been low, a few hundred degrees C at the most, compared to about 1000°C in other CVD processes.⁵ The lower temperature would mitigate the problems of substrate properties such as thermal stability and coefficients of expansion matching that of the deposited film. When compared to glow discharge deposition from silane,⁶ the flux of reactant to the surface can be far greater with the jet than in the conventional static systems under study. A process is envisioned in which the substrate is moved under a series of slot nozzles producing a wide ribbon

of reactant jets directed at the substrate. The reactant would include dopants, e.g., BCl_3 or POCl_3 just as in the glow discharge work so that p or n type films could be laid down, one upon the other in a continuous process. Such a process could be very attractive for mass production. Of course the problem of efficient photovoltaic solar energy conversion by polycrystalline silicon, on which many others are working, must be solved for this to become a viable process. In this program, the conditions controlling the nature of the film and better characterization of the film will be pursued.

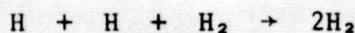
2. Production of SiHCl_3 from SiCl_4 . Preliminary experiments have yielded conversion efficiencies of about 15% of reactant SiCl_4 to SiHCl_3 . These conversions have occurred in liquid nitrogen traps and apparently not in the gas phase. In these experiments the traps were far downstream of the point of mixing SiCl_4 with the H/H_2 jet; under such conditions, the H-atom concentration at the traps is at most 20% of its original value (see Section II.B). Greater yields would thus be expected if the traps were moved closer to the point of mixing. Prior to pursuing this possibility, the observation that product formation occurs on the cooled surface and not in the gas phase must be substantiated. This can now be accomplished with greater confidence because of the improvements in the mass spectrometer for in situ sampling of the jet (see Section II.C). In addition, before further pursuing this possible process in any detail experimentally, studies to determine whether its economics are attractive compared to competitive processes will be undertaken.
3. Production of SiH_4 from SiHCl_3 . Experiments during this report period (see Section II.C) indicate that this process may occur.
4. Removal of metal impurities by nucleation. It has been consistently observed that larger deposits are more readily formed with technical grade than with semiconductor grade SiCl_4 .^{3,4} It has been hypothesized³ that this effect is due in part to metal impurities in technical grade SiCl_4 being ionized in the jet and acting as nucleation sites (see, however, Section II.C for an alternate explanation of these observations). Experimental verification of this hypothesis must be obtained and an economic evaluation of the process must be made. It might be conjectured that for this process, the identity of the discharge would not be

important (e.g., it could be N_2 or Ar rather than H_2). The non-equilibrium plasma jet would act only as a source of ions which charge transfer to the metal impurities in the $SiCl_4$ feed and cause them to nucleate.

B. H-ATOM DECAY

The rate of H-atom decay through the apparatus, Fig. 1, has been calculated assuming three-body recombination and reaction on the walls.

For the three-body recombination



with H_2 in excess:

$$\frac{c_H}{c_H^0} = (1 + c_H^0 c_{H_2} k_H t)^{-1}$$

where:

c_H = concentration of H atoms at any time t

c_H^0 = initial concentration of H atoms at $t = 0$

c_{H_2} = concentration of H_2 , a constant

k_H = recombination coefficient for H atoms, given by Kaufman⁷ as

$$9.5 \times 10^{-33} \left(\frac{300}{T} \right) \text{ ml}^2 \text{ sec}^{-1}$$

For recombination of H atoms on the wall the decay of H atoms is given by:

$$\frac{c_H}{c_H^0} = e^{-k_w t}$$

where k_w = the wall recombination rate. When the process is diffusion controlled, there are two conditions, given by solving the flow equation.⁸

These are:

For plug flow:

$$k_w^p = \left(\frac{23.2}{d^2} \right) D_H$$

where:

- d = diameter of the duct
 D_H = diffusion coefficient for H atoms in H_2
 $= 1 \times 10^3 \left(\frac{T}{300} \right)^{1/2}$ at 1 Torr estimated from the diffusion coefficient of Ar in H_2 .⁹

For laminar flow:

$$k_w^L = \left(\frac{14.6}{d^2} \right) D_H$$

If the process is limited by recombination on the wall, i.e., if the flux of H atoms to the wall exceeds the wall recombination rate, the expression is¹⁰:

$$k_w = \frac{\gamma}{2d} \bar{c}$$

where:

- γ = wall recombination coefficient for H atoms
 $\approx 10^{-3}$ (300-700 K) for quartz¹¹
 $= 2 \times 10^{-5}$ (300 K) to 5×10^{-4} (200 K) for Pyrex¹¹
 \bar{c} = molecular velocity $(8kT/\pi m_H)^{1/2}$

The time, t , to be used in these equations is given by:

$$t = \left(\frac{P_d}{\dot{n} RT} \right) \left(\frac{\pi d^2}{4} \right) l$$

where:

- P_d = pressure
 R = gas constant
 \dot{n} = molar flow rate of H_2
 l = length of duct.

For runs 11-18 (Table I of Ref. 2) in which products were collected in liquid nitrogen traps, the decay of H atoms prior to reaching the traps can be estimated from the above. For these experiments (cf. Fig. 1),

- P = 35 Torr
 T = 380 K, calculated for the jet
 c_H^0 = 1%, $6.8 \times 10^{15} \text{ ml}^{-1}$
 \dot{n} = 64 millimol sec^{-1}

To calculate the flow time it was assumed that the jet breaks up in about 15 cm and completely fills the tube. The flow time to the first liquid nitrogen trap then becomes about 69 millisec. The reduction in H-atom concentration by the time the flow reaches the first liquid nitrogen trap is then, for each of the various decay processes, operating independently of the other:

	c_H/c_H^0
Three-body recombination	0.29
Recombination on the wall	
Plug flow	0.13
Laminar flow	0.26
Wall recombination limited	
Pyrex	0.86
quartz	0.19

Since silicon, polymers and some SiO_2 are deposited on the wall, it may have a γ larger than any given above. The flow is probably more closely approximated by plug flow than by laminar flow. Thus by the time the first liquid nitrogen trap is reached the H-atom concentration has decayed to less than 20% of its initial value.

This means that the 10% to 15% conversion² of SiCl_4 to SiHCl_3 previously suggested as occurring on the walls of the liquid nitrogen trap took place after the H-atom concentration had decayed to $< 20\%$ of c_H^0 . Thus, greater yields should be obtainable by moving the traps closer to the nozzle. Such experiments will be carried out as time permits.

C. MASS SPECTROMETRIC ANALYSIS

In the last quarterly report,² we summarized the difficulties encountered with the simple magnetic mass spectrometer with which we planned to make in situ measurements and stated that a more sophisticated quadrupole instrument would be used to resolve the problems. Prior to pursuing this course, in situ sampling was carried out in the jet of a H/H_2 stream with SiHCl_3 injected in countercurrent flow.³ The results, Table I, while not directly reducible to product concentrations, indicate $\approx 40\%$ of the SiHCl_3 has reacted and the trend in the values from $\text{SiCl}_3^+ + \text{Si}^+$ indicates the formation of more highly hydrogenated products, especially silane. Similar

experiments with SiCl_4 , reported previously,^{1,3,4} did not give any indication of reaction by this technique. It was also observed that heavier coatings of solid product were obtained with SiHCl_3 than with SiCl_4 .

In another experiment to confirm the above, a gas sample was collected in an evacuated one liter flask ≈ 150 cm downstream of the nozzle and taken to the quadrupole mass spectrometer for analysis. The results, Table II, again indicate 30% to 40% loss in SiHCl_3 reactant, consistent with an increase in HCl , but no indication of the formation of more highly hydrogenated chlorosilanes.

Because the magnetic mass spectrometer was designed to operate at a fixed electron energy of 70 eV, the quadrupole instrument was used to measure the cracking patterns of the three chlorosilanes, SiCl_4 , SiHCl_3 , and SiH_2Cl_2 as a function of electron energy. The cracking patterns were distinctively simplified as the electron energy was decreased, Table III. The magnetic instrument was thus modified so that the electron energy could be varied. However, experiments with reduced electron energies indicated that a severe loss in sensitivity accompanied such a reduction. A compromise electron energy of 50 eV provides both good selectivity between the masses of interest and satisfactory sensitivity. Other modifications included the addition of a circuit to the linearly swept magnet supply (used for scanning the mass range); this circuit permits skipping of mass regions while sweeping over four pre-selected regions at a slow rate. At this slower sweep rate more electronic filtering can be used and, because only a small total mass range is actually measured to obtain all the chlorosilane peaks, more sweeps can be made during a run and the precision of the measurements can be increased by averaging.

Part of a calibration, consisting of two to four measurements per peak, is given in Table IV together with calculated relative intensities based on isotope ratios of Si and Cl. For the calculated intensities, one constant is fit for each chemical species, e.g., masses 63 and 67 require three constants for SiCl_2H_2 (for the three species SiCl , SiHCl and SiH_2Cl_2), two constants for SiCl_3H and one constant for SiCl_4 .

From the calibration data for the three chlorosilanes available it is apparent that differences in the three spectra are great enough and the results precise enough to permit the determination of relatively small amounts (a few percent) of one chlorosilane in the presence of others. Rather than

use only as many mass peaks as the number of species to be identified, most of the spectrum will be used in a least-squares fit for the three species for which calibration data are available. It is likely that if any SiH_4 or SiClH_3 is produced, its presence will be detected by lack of internal consistency of the data as was the case with finding a $\approx 3\%$ SiHCl_3 contribution in the SiCl_4 (technical) spectrum. The actual amount of SiHCl_3 present in the SiCl_4 is not known at this time since the calibrations were made relative to an ionization pressure gauge to which SiCl_4 and SiHCl_3 may respond differently. Since SiHCl_3 has been demonstrated to react more rapidly than SiCl_4 this impurity in the SiCl_4 may account for the difference in observed reaction rates for technical and semiconductor grade SiCl_4 .

Prior to using the mass spectrometer for analysis, a more thorough calibration will be carried out to increase the precision of the numbers and obtain information on the long-term stability of the instrument response.

D. SILICON FILM DEPOSITS

Experiments have been carried out to determine the characteristics of product films, assumed to be amorphous or polycrystalline silicon, and to determine the effect on these films of the chlorosilane reactant and the exposure time. For the entire series of experiments, the H/H_2 jet conditions were fixed and the downstream pressure was held essentially constant. Three or four ordinary microscope slides, 7.62×2.54 cm, were placed lengthwise along the bottom of the synthesis region section of the apparatus (70 mm i.d.). Both Pyrex and Vycor (quartz) slides were used. The chlorosilane was brought into the apparatus through a stainless steel tube (4.7 mm i.d., 6.4 mm o.d.) which was 2.9 cm off-center of the H/H_2 jet; thus a reactant jet of velocity varying from 160 cm sec^{-1} to 5800 cm sec^{-1} , depending upon feed rate, impinged on the nozzle holder plate. This produced a turbulent diffusive mixing with the H/H_2 jet which visually extended up to about 30 cm downstream of the H/H_2 nozzle face plate. It was in this region that deposits were collected on the slides. The deposits seemed to be symmetrically distributed around the walls of the reaction tube.

The conditions of the experiments were very close to*:

Nozzle No. 2

Hydrogen flow rate, millimol sec^{-1}	54
H-atom concentration, % H_2	3
Upstream discharge pressure, P_u , Torr	75
Downstream reaction chamber pressure, P_d , Torr	18
Discharge voltage, kV	780
Discharge current, amperes	2.1
Discharge power, Watts	1650
H/ H_2 jet temperature, K	
Static	440
Stagnation	670
H/ H_2 jet velocity, m sec^{-1}	2.6×10^3

Microscopic examination was made of the sample slides in most runs. Survey scans were taken of the slides by eye to ensure that the photomicrographs prepared were qualitatively representative of the surfaces.

In the first set of runs three Vycor slides were placed on the bottom of the reactor, the first against the nozzle plate, the second separated by 1.3 cm from the first and by 5.1 cm from the third. These runs, with some observations, are summarized in Table V. In all cases the maximum deposit was observed on the second, i.e., center slide, and the deposit appeared to follow a Gaussian distribution. In this set of runs the weight of the deposit was determined only for runs 116, 117 and 119 because the weights were observed to increase rapidly while weighing and thus thought to be meaningless. (See below, however, for a more complete discussion of this problem.) For the three runs in which a weight was obtained the following can be deduced:

* Some variation in downstream pressures was observed because the 70 $\ell \text{ sec}^{-1}$ vacuum pump was on its last legs. This pump has since been replaced by a new 140 $\ell \text{ sec}^{-1}$ pump.

Reactant	Run	Total Weight ^a of Deposit (g)	Rate of Deposit (mg sec ⁻¹)	Conversion Efficiency mol % Reagent as Silicon
SiCl ₄ (Technical)	116	4.2	0.79	8
SiCl ₄ (Semiconductor)	117	1.4	0.25	3
Silane	119	0.21	0.70	7

^a Estimating the weight deposited between the slides and assuming the deposit on the reactor tube has the same density as that on the slide.

In another set of experiments the SiHCl₃ flow rate was varied over a large range to determine the effect of equivalence ratio on the nature and quantity of deposit. Four Pyrex slides were placed end on, butting against the nozzle plate and touching each other. The slides were prepared by washing in trichloroethylene, dipping in 20% HF solution for approximately 10 sec, rinsing with distilled water, and drying with a paper towel. All other conditions were the same as in the above set of runs. The results were somewhat surprising in that, at least visually, the heaviest deposits occurred at the lower flow rates where a dark brown adhering film was formed. At intermediate flow rates the deposit appeared lighter and at the higher flow rates the character of the deposit was different, showing a gray metallic luster and strong adhesion to the surface. The basic data with descriptions of the observations are summarized in Table VI. Most of the coatings occurred on the central two slides (\approx 8-24 cm downstream), except at 5, 6, and 7.7 ml sec⁻¹ where the light coatings observed were mostly deposited on the second slide (\approx 8-16 cm downstream). Interpretation of these data in terms of effect of composition is complicated by uncertainties in the flow pattern in the reactor; the results are recorded here for future reference and as examples of the variations in coatings which might be obtained--their significance will, we hope, become evident as the program progresses.

1. Effect of Heating Deposits

By heat treating the deposits and observing the morphological changes or chemical changes, e.g., by gas evolution, it should be possible to determine the nature of the surface.

A simple heat treating furnace was constructed which permits heating slides with deposits in a carrier gas stream up to 1250 K. The oven consists of a resistively heated (25 cm heated zone) insulated 4.1 cm i.d. x 58 cm ceramic tube. Bath gas is preheated in a stainless steel tubing coiled around the heated section; for flow rates of 2 cc sec^{-1} , a temperature of 620 K is obtained with a 60 W power input, and 1250 K with 375 W input. Temperatures are constant to better than 0.5% for extended periods of time. The silane/H/H₂ reaction deposit was heated in the oven with nitrogen flow for 26 hr at 830 K; a photomicrograph is shown in Fig. 2. Before heating the surface looked like a structureless fine powder. After heating the surface appeared as a white film and exhibited some microscopic structure (Fig. 2). There was no significant weight change on heating.

A sample of solid product from the semiconductor grade SiCl₄/H/H₂ reaction (run 122 Table V) was heated to 820 K for 22 hr and the results are displayed in Fig. 3. Prior to heating the coating had a lustrous metallic appearance which dulled on heating. Some parts of the slide showed small cracks on heating, others did not. Generally the number density of spheres, which we tentatively identify as polycrystalline silicon appeared to increase on heating. Heating did not change the weight. Technical grade SiCl₄ deposits gave similar effects on heating; Fig. 4 shows the effect of heating (820 K, 24 hr) on the deposit of run 124 (cf. Table V). The dulling of the surface upon heat treatment is noticeable in the reflected light photomicrographs of Figs. 3 and 4. The dark brown deposits from SiHCl₃ (run 128, Table V, and run 136, Table VI) showed the same polycrystalline structure as in Fig. 3. The slide from run 136 was heated to 820 K for 24 hr and again very little change was noted.

The results of heating the visually very light shiny metallic deposit from SiHCl₃ (run 133 Table VI) to 820 K for 24 hr is shown in Fig. 5. The black areas are holes in the deposit which appear to increase in size on heating.

2. Rates of Silicon Film Formation

In many of the runs in which solids were collected on slides placed in the bottom of the reactor the weight collected during the course of the

experiment was determined as a matter of course. After removal of the slides from the reactor, these weights always showed an increase with time due, we assumed, to the hygroscopic nature of the surface. If water reacts with any $(-\text{SiH}_x\text{Cl}_y-)_n$ type polymer to release HCl , a weight loss should occur due to the replacement of Cl by O . On the other hand, a highly hydrogenated silicon polymer such as $(-\text{SiH}_2-)_n$ might react with air to give SiO_2 or, in the presence of alkali on the surface, it might hydrolyze to $(-\text{SiHOH})_n$, thereby gaining weight.

An experiment was thus carried out to more carefully determine the nature of the weight gain. A Vycor slide was placed on the bottom of the reactor and exposed to the reacting gases as above. The experimental conditions were:

Upstream discharge pressure, Torr	66
Downstream reaction chamber pressure, Torr	25
Discharge power, Watts	1,000
Run time, min	110

The freshly prepared slide exhibited a weight gain of ≈ 2 mg within the first $\approx 1/2$ hr after removal from the reactor. Sitting in air for ≈ 11 hr resulted in a 6 mg weight loss, while oven heating (400 K and 670 K) and air cooling had no net effect (i.e., weight was lost on heating and gained on cooling). It is concluded that the samples are simply absorbing and desorbing moisture from the atmosphere and that the accuracy of the sample weight determination is within $\pm 15\%$.

In light of this some of the previously recorded deposit weights from SiHCl_3 runs have been plotted as a function of SiHCl_3 flow rate, Fig. 6, assuming the deposit to be silicon. These curves yield a rate of deposition of $4 \mu\text{m min}^{-1}$ (assuming the deposit has the density of silicon) at a conversion efficiency of 17% and an equivalence ratio of 0.4 (SiHCl_3 flow 9 millimol min^{-1}). One implication of the low equivalence ratio* is that the hydrogen atoms are not being efficiently utilized, or that the reaction requires more than four hydrogen atoms per molecule of SiHCl_3 reacting (cf. Ref. 1, Section II.A.3).

* As defined in Table V.

3. Effect of Substrate Exposure Time

A set of experiments was carried out in which the time the slides were exposed to the reactants was varied. Samples were collected and handled as in the above tests. Four preweighed Vycor microscope slides (7.6 cm x 2.5 cm) were laid end-to-end in the synthesis region. Slide 1 touched the nozzle (anode) holder flange; the remaining slides were numbered 2, 3, 4 in the downstream direction. The discharge conditions in these experiments were as given on page 9 and the flow rate of SiCl_4 (technical grade) was fixed at $0.34 \text{ millimol sec}^{-1}$. Exposure times of clean sets of slides to the reaction were varied from 3-27 min. In addition to these runs, some exposed slides were heat treated, re-exposed to the reaction, or exposed only to the discharge. Upon completion of a run, the slides were removed from the reactor and allowed to cool in air for 10-15 min and weighed. Visual inspection of the slides using the metallurgical microscope was made in a preliminary fashion at this time as well. Display photomicrographs were made as convenient.

The rate of solid deposition was observed to be constant as indicated by the data of Table VII and Fig. 7. From the figure it can be seen that the deposits are symmetric about the center of the four slides, with slides 1 and 4 and slides 2 and 3 being equivalent. The deposition rates derived from Fig. 7 are 0.27 mg min^{-1} for slides 1, 4 and 0.72 mg min^{-1} for slides 2, 3. Assuming that the deposits on slides 2 and 3 are uniform in thickness, the films collected range in thickness from $0.5\text{--}4.5 \text{ }\mu\text{m}$. These data yield a rate of film deposition of $0.2 \text{ }\mu\text{m min}^{-1}$, assuming the deposit has the density of silicon. The thinner films, when seen with the naked eye (3 and 6 min), show interference fringes. At least two green fringes are apparent on the 3 min exposure and five on the 6 min exposure slide. Classical theory gives

$$\text{thickness} = \frac{(\text{no. of fringes} + 1/2) \cdot \text{wavelength}}{2 \cdot \text{refractive index}}$$

Taking the wavelength $\approx 5.5 \times 10^{-5} \text{ cm}$ (green light) and refractive index ≈ 1.5 gives a film thickness of $0.5 \text{ }\mu\text{m}$ for the 3 min exposure and $1.1 \text{ }\mu\text{m}$ for the 6 min exposure, consistent with the above calculation based on uniform film thickness.

Again assuming that the deposits are pure Si, and using the observation that solid deposits in the synthesis region are cylindrically symmetric about the H/H₂ jet axis, the yields of solid are estimated for the runs in which no peeling was observed, Table VII. The solid product yield from SiCl₄ for these conditions is between 3% and 4%.

Two types of deposit are observed, a glassy film (assumed to be amorphous Si) and metallic particles (assumed to be polycrystalline Si). From the photomicrographs, Fig. 8, the presence of many small particles can easily be seen. The glassy film is more evident when cracks appear in it at the longer exposure times. At short exposure times very few particles and many small holes (bright spots on photomicrographs--see Fig. 8) can be seen. This suggests that the particles are embedded in the films. It appears on observation with the metallurgical microscope that the particles fall onto the surface from the gas stream and are slightly mobile until they are covered by the glassy film. Indeed, separate experiments, in which surfaces were made "stickier" by coating the slides with vacuum grease, clearly showed the presence of many particles after only 3 min exposure. We tentatively conclude that both types of Si are being formed simultaneously at all reaction times. It should also be noted that the buildup of deposits with time can be seen from the progressive darkening of the constant exposure photomicrographs of Fig. 8.

Heat and/or a thick film produces fractures of the glassy films into plates and evidently leads to peeling of the deposits. Strongly heating a thin deposit (9 min exposure to the reaction, Fig. 8) to 1220 K for 2.5 hr in an Ar atmosphere is sufficient to completely fracture the deposit into small plates probably due to the difference in thermal expansion coefficients between the film and slide. The small increase in optical density of the deposit on heating possibly suggests a phase change to polycrystalline Si. The milder heating effect of the discharge/reaction begins to form small cracks by ≈ 15 min exposure time. By 21 and 27 min exposure time fracturing is severe enough for the deposits to peel away from the slides. The cracks seem to propagate between particles; see, e.g., Figs. 8 and 9.

Upon heating to 1220 K in an Ar atmosphere, the brown glassy films take on a gray metallic luster by reflected light. The films remain translucent and transmit an amber color from white light. The transmitted light

decreases for slides after heating, an effect which is illustrated in Fig. 9 where exposure time had to be doubled in order to make out details on the strongly heated, two step exposure 27 min slide. This effect is also noticeable in the 9 min exposure of Fig. 8.

One major objective in this set of experiments was to determine the variation in particle size and number density with the time of substrate exposure. Qualitatively the metallic particles are uniform in size ($\approx 0.5\text{--}1.0\ \mu\text{m}$) independent of exposure time. The number density of deposited particles increases with time, see Fig. 8. Larger particles appear to result from agglomeration on the surface; see the scanning electron micrographs, SEM, Fig. 10. Qualitative results have not yet been obtained because of difficulties in obtaining counts of particles and particle sizes from photomicrographs at the required high magnification.

III. CONCLUSIONS

The following conclusions are drawn from this period's work:

1. Four processes utilizing the non-equilibrium plasma jet merit further consideration:
 - a. Production of polycrystalline silicon photovoltaic surfaces.
 - b. Production of SiHCl_3 from SiCl_4 .
 - c. Production of SiH_4 from SiHCl_3 .
 - d. Purification of SiCl_4 by metal impurity nucleation.
2. In the present reactor H-atom concentration decays to less than 20% of its initial value by the time it reaches the liquid nitrogen traps. Thus the 10 to 15% yields of SiHCl_3 obtained from SiCl_4 should be increased by moving the traps closer to the nozzle.
3. Both amorphous and polycrystalline films of silicon which adhere very tightly to Pyrex or 7ycor are laid down, sometimes simultaneously, from SiCl_4 or SiHCl_3 . SiH_4 did not produce a strongly adhering film.
4. Maximum conversion efficiencies (mol % reagent to product silicon) observed for film formation to date are: SiHCl_3 17%, SiCl_4 (technical) 8%, SiH_4 7%, and SiCl_4 (semiconductor) 3%.

5. The films are stable at temperatures up to 1200 K except for cracking and a change to a more metallic appearance, possibly associated with a change from amorphous to polycrystalline silicon.

IV. PLANS

During the next quarter we plan to: (1) determine the nature of the silicon films by using: X-ray fluorescence; particle induced X-ray emission, PIXE; electrical conductivity and scanning electron microscopy, (2) quantify the change in particle size and number density with time, (3) determine the extent of gas-phase reaction occurring using in situ mass spectrometer sampling, (4) modify the apparatus to simplify experiments and improve accuracy (this includes improving the mixing of the chlorosilane with the H/H₂ jet), and (5) carry out preliminary cost evaluation of the three processes.

V. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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TABLE I
 MASS SPECTROMETRIC STUDY OF $\text{H}/\text{H}_2 + \text{SiHCl}_3$
 Runs 112-113
 Nozzle No. 2 $P_u^\circ = 50$ Torr, $P_d = 20$ Torr

SiHCl_3 Flow (ml sec ⁻¹)	Discharge Power (kW)	Probe Distance (cm)	Change in Signal from Discharge "Off" to Discharge "On" (%)			
			SiCl_3^+	SiCl_2^+	SiCl^+	Si^+
1.2	1.2	21	-50	-20	-50	+100
5.9	1.0	29	-40	-60	-40	---
		51	-10	-10	-10	---
	2.0	29	-70	-80	-70	---
		51	-60	-50	-50	---
6.1	1.2	21	-30	-30	-20	+100
		51	-50	-40	+10	+100
12.2	1.2	21	-30	-10	-30	+60
		36	-30	-20	-30	+10
		51	-60	-40	-30	-10
		Averages	-43	-36	-32	+36

TABLE II
MASS SPECTROMETRIC STUDY OF $\text{H}/\text{H}_2 + \text{SiHCl}_3$

Run 115

Nozzle No. 2 Discharge Power = 1 kW

H_2 flow = 54 millimol sec^{-1}

SiHCl_3 flow = 0.42 millimol sec^{-1}

H-atom concentration = 2.5%

P_u = 67 Torr

P_d = 24 Torr

Quadrupole Mass Spectrometer. Electron Energy = 26 eV

Ion	Relative Intensity at Mass				
	133 <u>SiCl_3^+</u>	98 <u>SiCl_2^+</u>	63 <u>SiCl^+</u>	36 <u>HCl^+</u>	38
Discharge "On"	56	41	14	---	----
"Off"	58	67	18	---	----
Change in Signal from Discharge "Off" to Discharge "On"	-34	-39	-22	---	----
Discharge "On"	90	41	10	91	36
"Off"	132	110	38	30	8.8
Change in Signal from Discharge "Off" to Discharge "On"	-32	-63	-74	200	310

TABLE III
EFFECT OF ELECTRON ENERGY ON THE CRACKING PATTERN
OF CHLOROSILANES^a

	Electron Energy (eV)	Relative Intensity at Mass			
		170	133	98	63
		SiCl_4^+	SiCl_3^+	SiCl_2^+	SiCl^+
SiCl_4	73	0.35	1.00	0.13	0.55
	26	1.00	0.98	0.04	0.18
	18	1.00	0.55	---	---
SiHCl_3	73	---	1.00	0.14	0.95
	26	---	1.00	0.37	0.04
	18	---	1.00	0.28	0.03
SiH_2Cl_2	73	---	---	0.42	1.00
	26	---	---	1.00	0.48
	18	---	---	1.00	0.16

^a The 73 eV data was taken with the magnetic mass spectrometer and the 26 and 18 eV data were taken with the quadrupole mass spectrometer.

TABLE IV
SELECTED MASS SPECTRA OF SiH_2Cl_2 , SiHCl_3 , AND SiCl_4 ^a

Mass	SiH_2Cl_2		SiHCl_3		SiCl_4		
	Measured	Calculated	Measured	Calculated	Measured	Calculated	Calculated ^b
63	5.42	5.43	4.52	4.52	2.07	2.07	2.07
64	3.81	3.82	0.45	0.45	0.12	0.10	0.11
65	8.88	8.88	1.59	1.63	0.74	0.74	0.74
66	1.67	1.70	0.16	0.15	0.02	0.03	0.04
67	2.54	2.54	0.06	0.05	0.01	0.02	0.02
98	2.38	2.36	2.80	2.80	0.37	0.37	0.37
99	9.84	9.84	2.53	2.53	0.09	0.02	0.08
100	2.11	2.12	1.91	2.04	0.24	0.25	0.25
101	6.47	6.73	1.67	1.72	0.06	0.01	0.05
102	0.64	0.62	0.44	0.43	0.05	0.05	0.05
103	1.15	1.25	0.31	0.32	0.01	0.02	0.03

^a Measurements taken with magnetic mass spectrometer.

^b Calculated by adding 3.1% of SiHCl_3 intensities to calculate SiCl_4 intensities.

TABLE V
SOLID DEPOSITION EXPERIMENTS

Runs 116-131

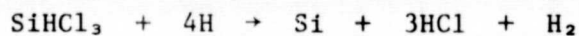
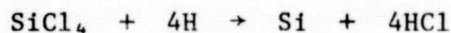
Chlorosilane or Silane Feed at 7.7 ml sec^{-1} , Vycor Slides

Run	Reactant	Equivalence Ratio ^a	Run Time (min)	Relative ^b Deposit	Observations
119	SiH ₄	0.43	5	3	Jet white with some green for $\approx 15 \text{ cm}$, orangish-brown talc like deposit, rubbed off easily, not hygroscopic.
124	SiCl ₄ (Technical)	0.85	15	3	Dull brown with gray cast strongly adherent.
126			30	4	Shiny gray-brown deposit which flaked away, appeared to be dull gray deposit over a glassy brown deposit.
125			60	4	Flaky deposit like run 126, but more flaky.
116			90	4	Flaky deposit.
120	SiCl ₄ (Semiconductor)	0.85	15	2	Glassy brown strongly adherent.
123			15	1	Very little coating compared to run 120. New package of slides with finger smudges, cleaned with trichloroethylene. ^c
122			30	3	Brown with dull gray cast strongly adherent.
121			60	4	Similar to run 122 but appears less dense, strongly adherent.

TABLE V (continued)

Run	Reactant	Equivalence Ratio ^a	Run Time (min)	Relative ^b Deposit	Observations
129	SiHCl ₃	0.85	3.3	1	Brown deposit, not very adherent.
128			7.5	3	Dark brown shiny deposit which flaked off.
130			7.5	2	Slide exposed in center of tube, end on to jet.
131			7.5	2	Similar to run 128 but more flaky.
127			15	3	Similar to run 128 but more flaky.

^a Equivalence ratio, ϕ , defined as $\phi = \frac{(\text{chlorosilane or silane/H})_{\text{actual}}}{(\text{chlorosilane or silane/H})_{\text{stoic}}}$ where it is assumed that the stoichiometric reaction is:



^b Visual inspection. 1-4 for light to heavy.

^c Prior to run 123 slides were cleaned with a paper towel; after this run they were cleaned with trichloroethylene and wiped with a paper towel.

TABLE VI
SOLID DEPOSITION FROM SiHCl_3
Runs 132-141
5 min Runs

Run	SiHCl_3 Flow (ml sec^{-1})	Equivalence Ratio	Observations
141	0.5	0.06	Heavy brown adhering deposit.
139	1.0	0.11	Heavy brown adhering deposit.
136	2.0	0.23	Less heavy brown deposit with tendency to flake.
134	3.9	0.43	Heavy brown adhering deposit.
140	5.0	0.55	Very light deposit, flaky.
137	6.0	0.66	Slightly heavier brown deposit than run 140.
132	7.7	0.85	Somewhat heavier brown deposit.
135	10	1.10	Metallic appearing thin deposit.
133	15	1.65	Light shiny thin metallic deposit appearing with large variation in density.
138	18	1.98	Similar to run 133.

TABLE VII
SOLID DEPOSITION FROM TECHNICAL GRADE SiCl_4
Runs 142-147
Vycor Slides

Exposure Time (min)	Weight Gain on Slide (mg)				Conversion Efficiency		Experiment No.
	1	2	3	4	mol % SiCl_4 as Si		
3	1.97	2.17	2.14	2.14	4.4		142
6	2.26	3.10	2.90	2.14	2.7		147
9	3.19	5.02	5.66	3.78	3.1		144
15	5.87	10.44	10.78	6.58	3.5		143
21	6.42	10.90 ^a	8.06 ^a	7.83	---		146
27	8.27	8.84 ^a	8.84 ^a	8.92	---		145

^a Peeling of deposits caused loss of material.

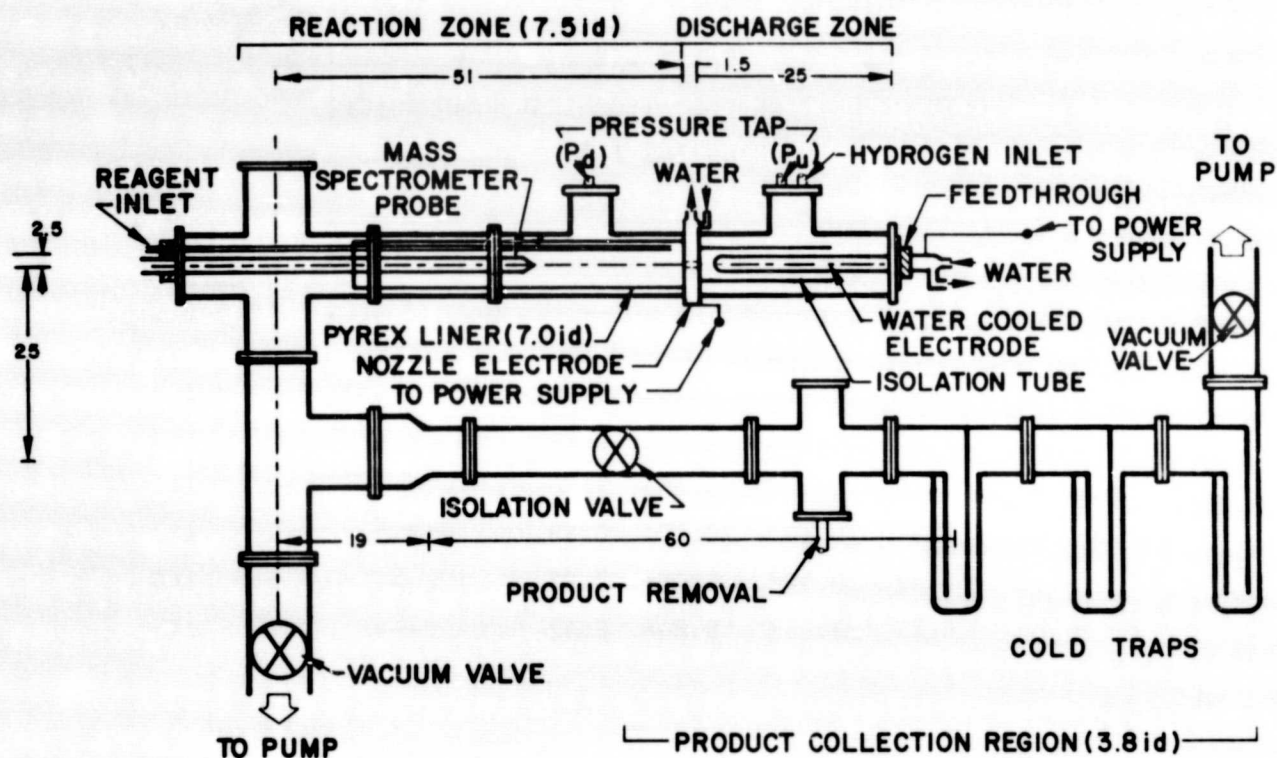
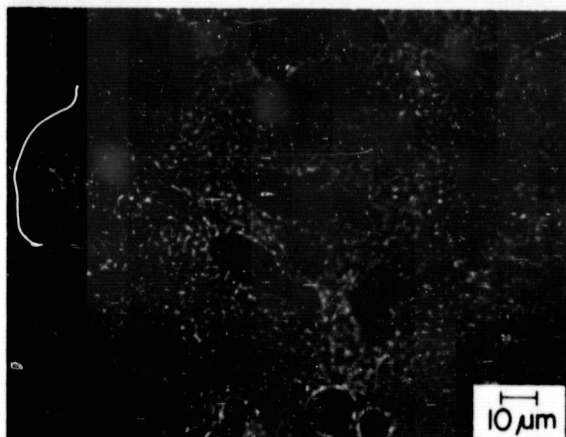
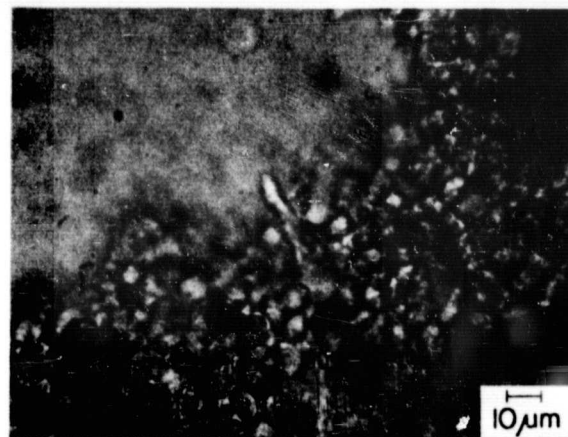


FIGURE 1 NON-EQUILIBRIUM PLASMA JET APPARATUS

Dimensions in cm



BEFORE HEATING



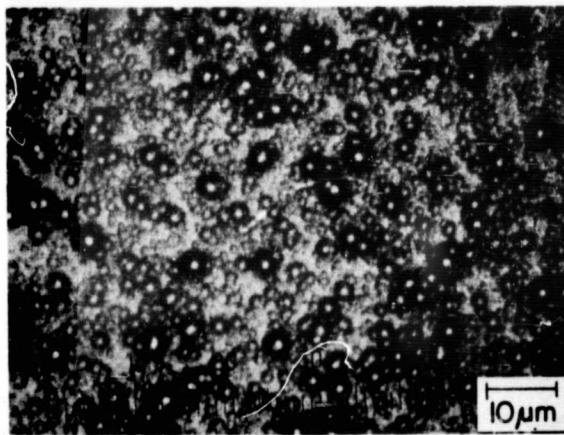
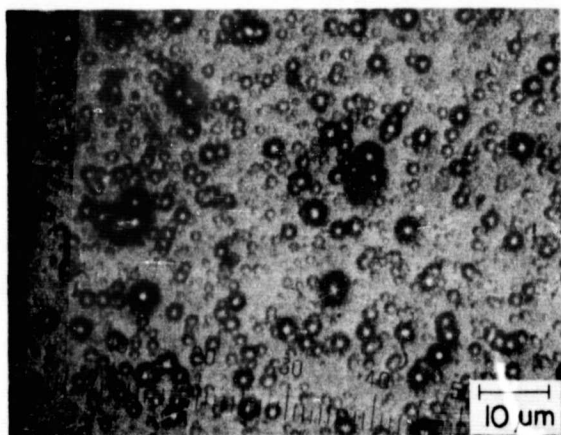
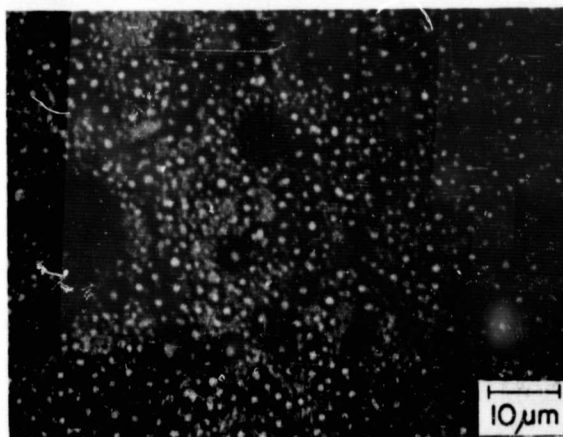
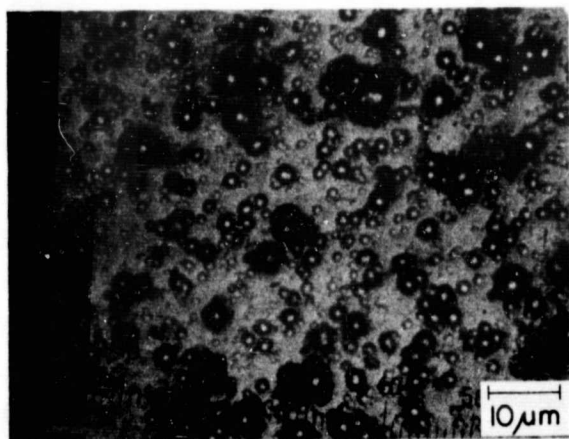
AFTER HEATING

FIGURE 2 EFFECT OF HEATING SILANE DEPOSIT TO 830 K FOR 26 HR

Run 119

Backlighting. Photographed at edge of deposit.

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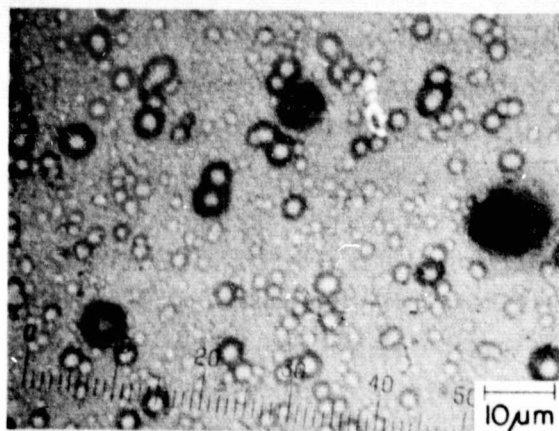
AFTER HEATING

FIGURE 3 EFFECT OF HEATING SEMICONDUCTOR GRADE SiCl_4 DEPOSIT TO 820 K FOR 22 HR

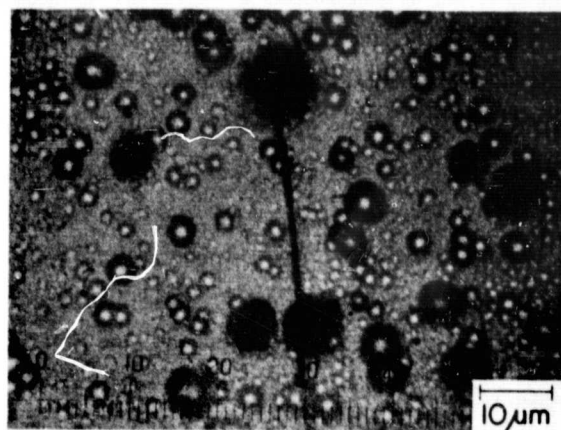
Run 122

Front lighting

Two sets of photographs because part of deposit cracked and part did not.



BEFORE HEATING

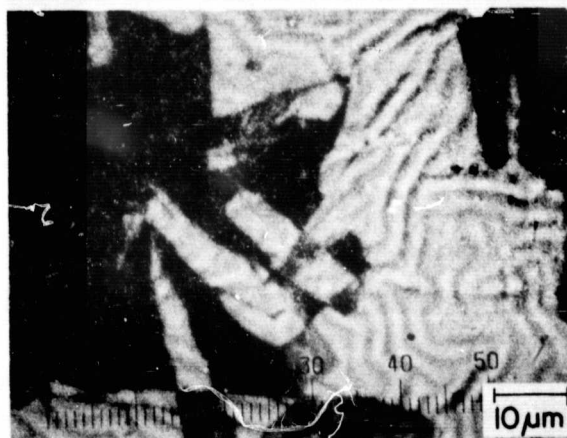
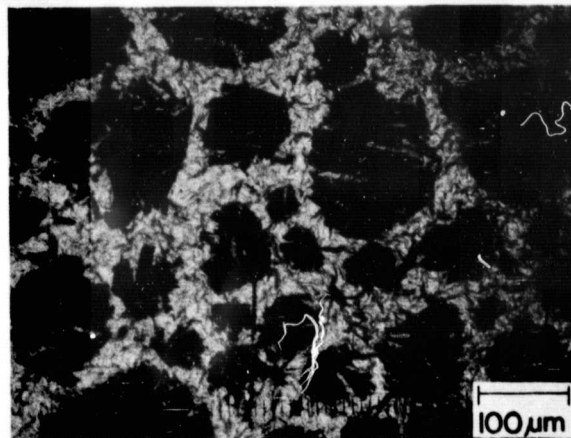
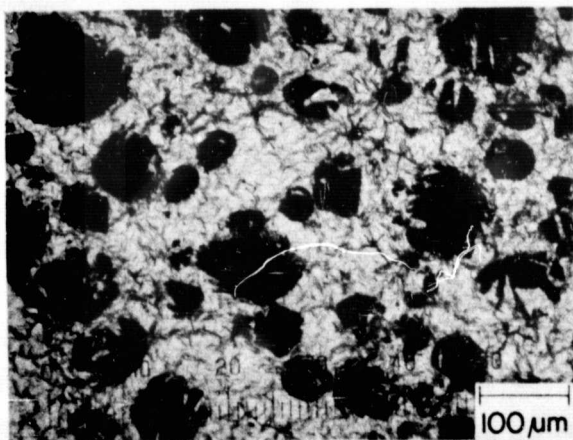


AFTER HEATING

FIGURE 4 EFFECT OF HEATING TECHNICAL GRADE SiCl_4 DEPOSIT
TO 820 K FOR 24 HR

Run 124
Front lighting

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BEFORE HEATING

AFTER HEATING

FIGURE 5 EFFECT OF HEATING SiHCl_3 DEPOSIT TO 820 K FOR 24 HR

Run 133

Front lighting

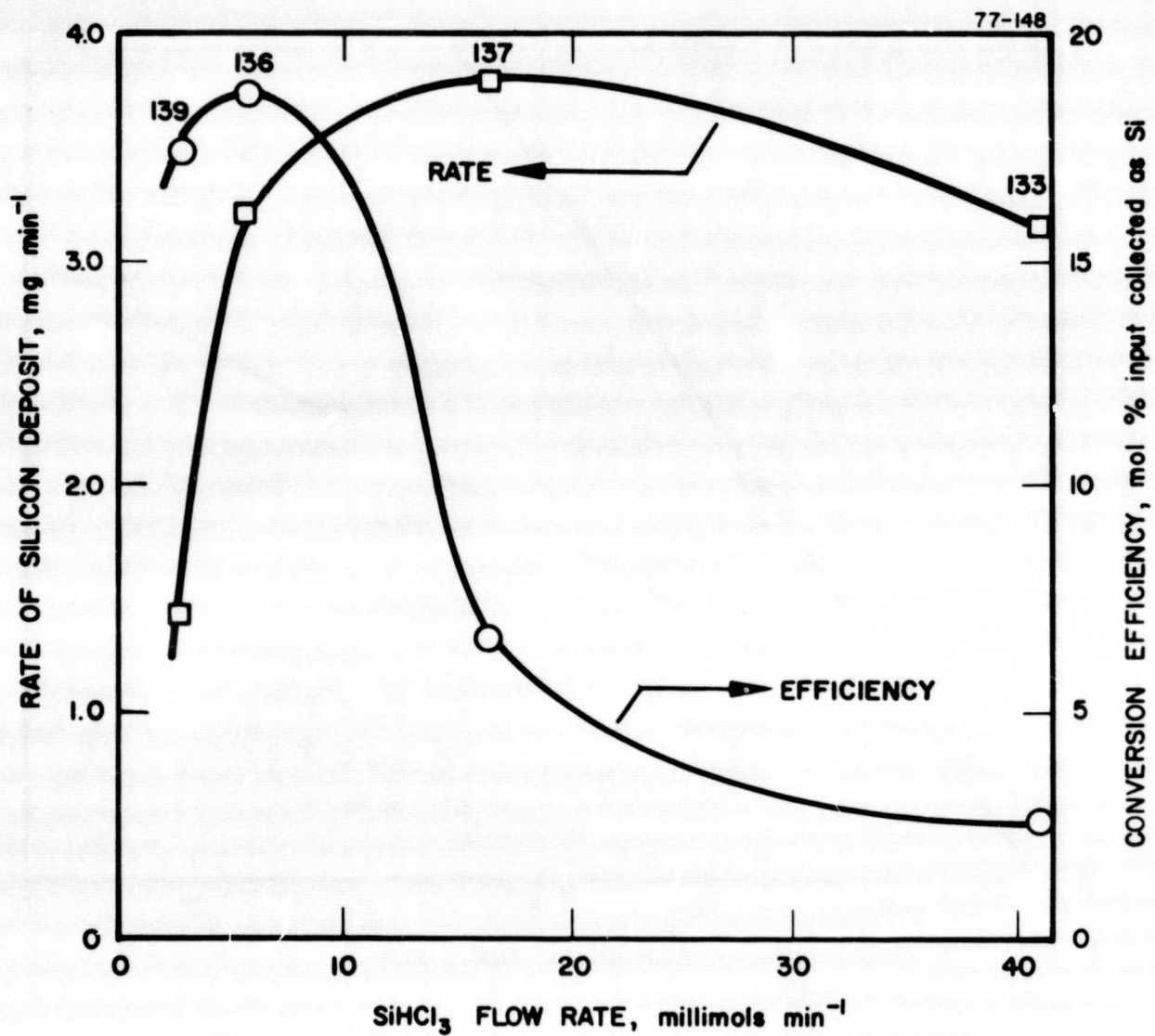


FIGURE 6 RATE OF SILICON DEPOSIT FROM SiHCl₃
Run numbers indicated above points.

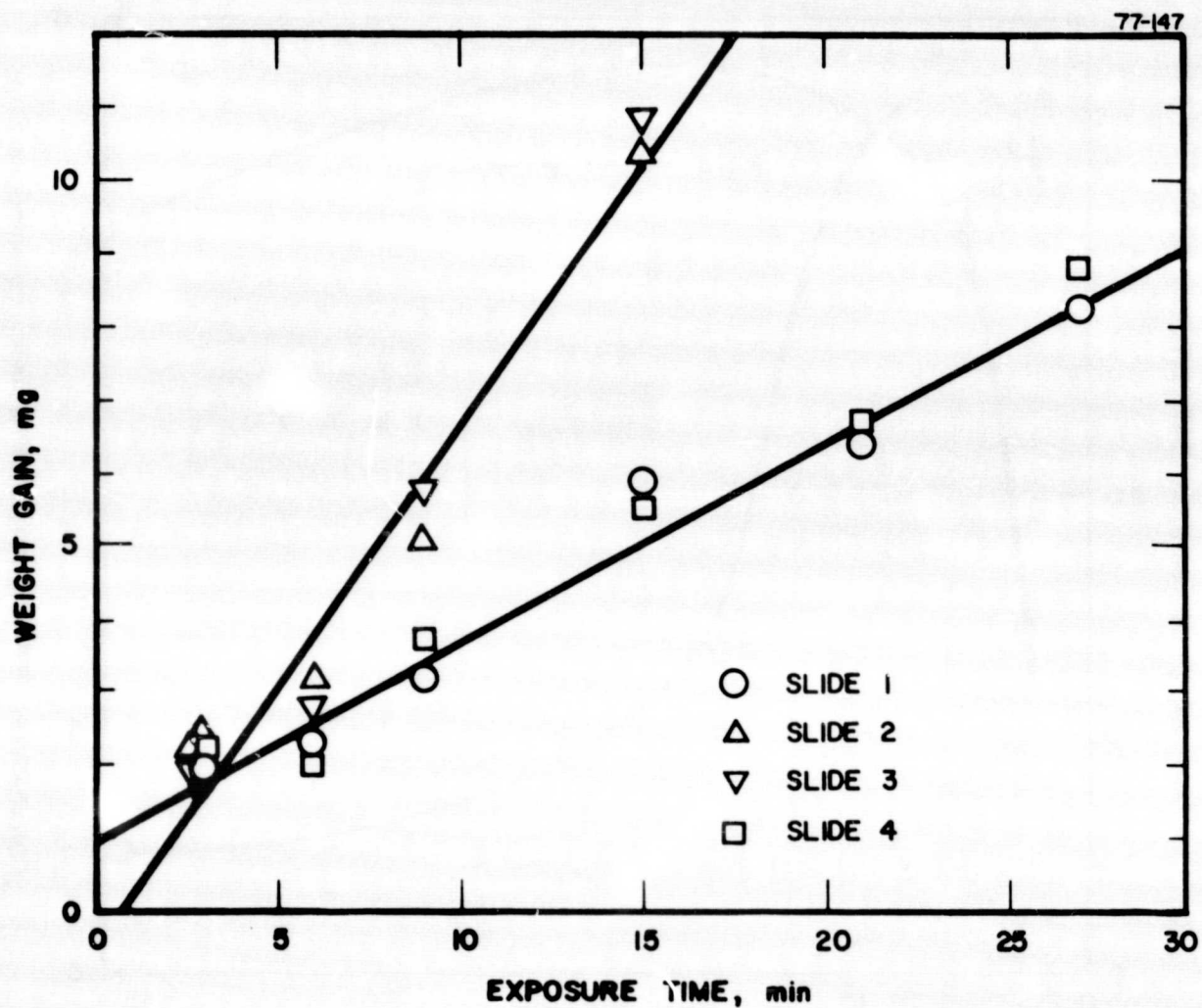
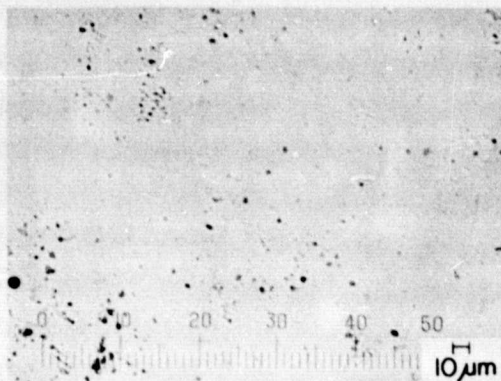


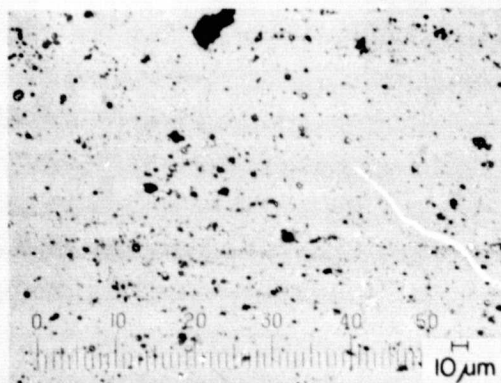
FIGURE 7 RATE OF SILICON DEPOSITION ON VYCOR SLIDES

Runs 142-147



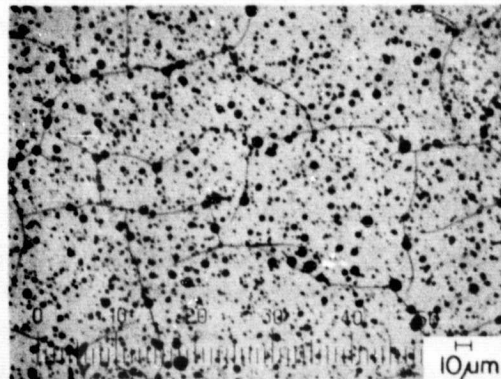
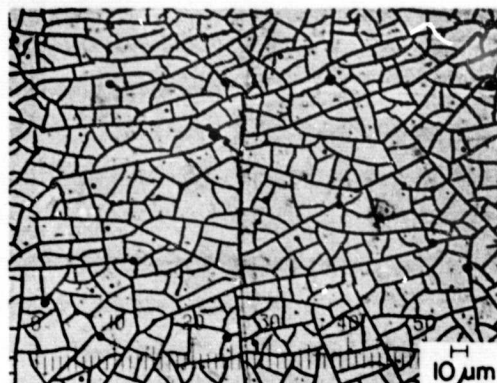
3 min

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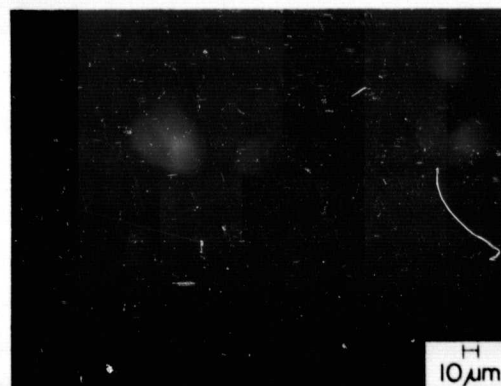


9 min

1220 K
for 2.5 hr



15 min



27 min

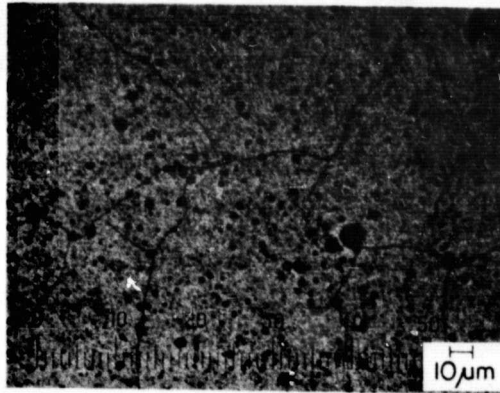
FIGURE 8 EFFECT OF EXPOSURE TIME ON
SILICON FILMS DEPOSITED FROM SiCl_4

Runs 142, 143, 144, 145, 151

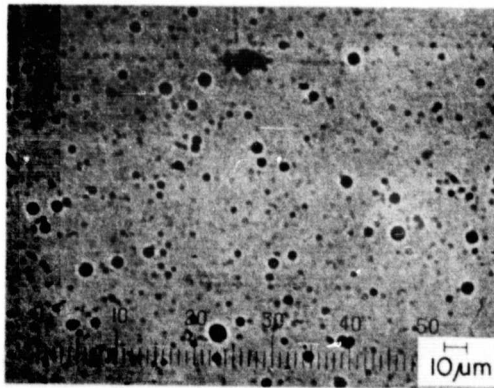
Reaction exposure period as
indicated at each photograph.

Bright field transmitted light.

Same photographic exposure time for
each photograph.

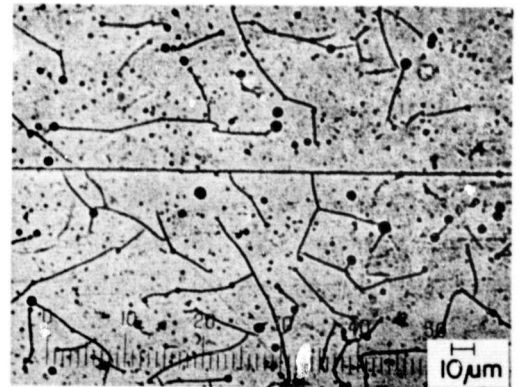


1/30 sec PHOTOMICROGRAPH
ONE REACTANT EXPOSURE PERIOD, 27 min



1/30 sec PHOTOMICROGRAPH

1220 K
for 2.5 hr



1/15 sec PHOTOMICROGRAPH

TWO REACTANT EXPOSURE PERIODS, 15 min + 12 min

FIGURE 9 EFFECT OF MULTIPLE EXPOSURES AND HEATING OF
HEAVY DEPOSITS

Runs 145, 149, 153
Total exposure to reactants, 27 min

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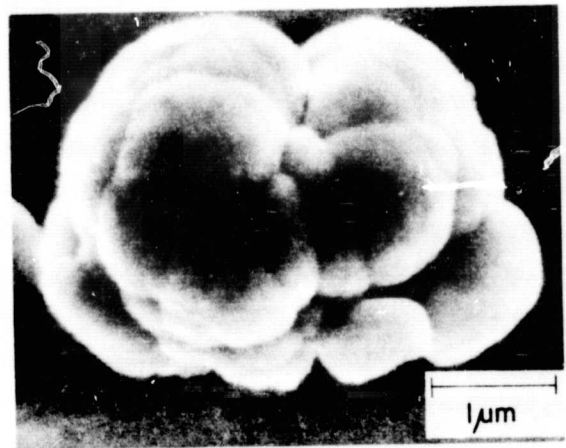
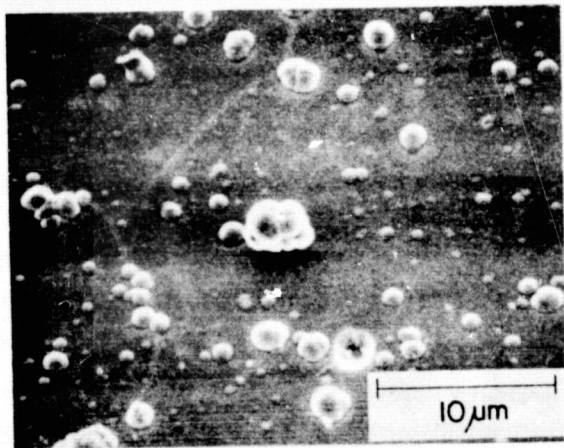


FIGURE 10 SCANNING ELECTRON MICROGRAPH OF TYPICAL
PARTICLE AGGLOMERATE

Run 145

Courtesy, Princeton Gamma Tech, Inc.